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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G02B 6/10, G01N 21/00

A1

(11) International Publication Number: WO 00/36442

(43) International Publication Date: 22 June 2000 (22.06.00)

(21) International Application Number: PCT/US99/24974

(22) International Filing Date: 25 October 1999 (25.10.99)

(30) Priority Data:
60/106,132 29 October 1998 (29.10.98) US

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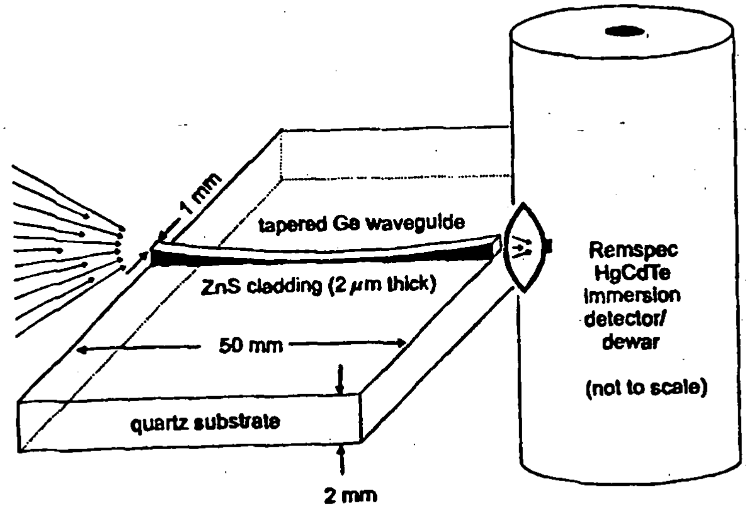
(81) Designated States: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: TAPERED QUASI-PLANAR GERMANIUM WAVEGUIDES FOR MID-IR SENSING

(57) Abstract

A quasi-planar waveguide for transmission of mid-IR sensing is disclosed. The Ge waveguide (172) is tapered from a thichness of 1mm at the ends to a minimum of 20-100 μ at the center. This tapering improves the efficiency of the optical coupling both into the waveguide from an FTIR spectrometer, and out of the waveguide onto a small-area IR detector (176). The tapering makes it possible to dispense with using an IR microscope couple light through the waveguide (172), enabling efficient coupling with a detector (176) directly coupled to an immersion lens. This optical arrangement makes such thin supported waveguides more useful as sensors, because they can be made quite long (e.g. 50 mm) and mounted horizontally. Furthermore, even with a 20-μ x 1-mm cross section, sufficient throughput is obtained to give signal/noise ratios in excess of 1000 over most of the 1000-5000 cm range, with just 2 min of scanning at 8 cm resolution. The small (0.02 mm) cross section of the waveguide (172) nevertheless yields great sensitivity to small numbers of IR-absorbing molecules near its surface.



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TAPERED QUASI-PLANAR GERMANIUM WAVEGUIDES FOR MID-IR SENSING

This work was supported by NSF grant MCB-9722887 to Mark S. Braiman.

Cross-reference to Related Patent Applications

The present application claims the benefits under 35 U.S.C. 119(e) of provisional patent application serial number 60/106,132, filed October 29, 1998. This application incorporates by reference, as though recited in full, the disclosure of parent application 08/874,711 and copending provisional patent application serial number 60/106,132.

Background of the Invention

Supported planar IR waveguides, having a thickness between 50-100 μm, have been fabricated by grinding and polishing single crystals of germanium. These thin planar Ge waveguides are useful as mid-IR evanescent-wave sensors. A significant portion of the light energy transmitted through such waveguides actually propagates outside the germanium, as an evanescent wave in the surrounding medium. With <100-μm-thick waveguides, a very small number of IR- absorbing molecules near the surface of the waveguide can significantly attenuate the light transmitted through the waveguide, allowing the measurement of an ATR (attenuated total reflection) spectrum. Sizable ATR bands are therefore observed from thin surface layers under 1 mm^2 in area. This includes thin coatings on small pieces of polymer film, as well as patches of the plasma membrane of large individual cells, e.g. frog oocytes.

One difficulty with using thin planar Ge waveguides as internal reflection elements (IREs) is coupling measurable amounts of light through such waveguides and onto a detector. Prior art requires the use of an IR microscope in order to measure useful spectra through waveguides having a thickness between 30-100 μm. Use of a microscope, however, results in significant limitations on the waveguide configurations that can be

used. In particular, waveguide lengths were generally limited to ~12 mm, the maximum separation between objective and condenser focal points on commercial FTIR microscopes. Furthermore, the waveguides had to be positioned vertically, i.e. along the optical axis of the microscope. This is an inconvenience for samples containing liquids, especially small biological samples.

Summary of the Invention

A quasi-planar waveguide, preferable made from single-crystal germanium, is disclosed wherein one of the surfaces has an arcuate contour while a parallel, second surface is planar, the first surface being concave relative to the second surface. The perimeter is comprised of multiple opposing planar surfaces at right angles to the second surface. The second surface is coated with a cladding, such as ZnS and then adhered to a substrate, such as quartz. The substrate must have a perimeter at least equal to that of the waveguide and a thickness sufficient to support the waveguide.

The arcuate surface of the waveguide has an apex at least about four times greater than the nadir, with a preferred ratio of nadir to apex taper of at least about 10 and up to about 50. The nadir of the waveguide is less than 100μm, and preferably in the range of 1 to 20μm. The arcuate surface is polished to about a 0.1 μm finish to prevent light scattering.

The tapered waveguide can be coupled directly to an IR detector, eliminating the need for a microscope and enabling more accurate alignment. The elimination of the microscope also enables the waveguide to be mounted horizontally. The tapered waveguide increases IR signal throughput by about 4-5 fold, a result of filling the large numerical aperture of a high-index waveguide medium (Ge, n=4). This increase, for a given sensor thickness, makes it possible to detect the IR signal level more precisely in a shorter length of time. With an untapered planar waveguide, the largest numerical aperture

that can be attained inside the waveguide is equal to the numerical aperture of the element that focuses light through air onto the end of the waveguide. This must always be less than 1, and for commercially available focusing optics is typically 0.5-0.8.

On the other hand, the fundamental limitation on the largest numerical aperture that can be propagated inside a dielectric waveguide is the refractive index of the waveguide material and it's cladding, and is equal to $(n_1^2-n_2^2)^{1/2}$. Here n_1 is the refractive index of the waveguide medium (n_1=4 for Ge), while n_2 is the highest refractive index of the cladding materials in contact with the waveguide (n_2 = 2.26 for ZnS). For the disclosed ZnS-clad Ge waveguide, this maximum numerical aperture is 3.3, or approximately 4-fold higher than the numerical aperture of available focusing optics. In theory, at least ~4-fold more light energy can be propagated through the sensing region of a planar Ge waveguide than can be obtained by focusing light through air into the edge of an untapered waveguide of the same minimum thickness. This theoretical maximum throughput is, in fact, closely approached with the tapered waveguide design.

Brief Description of the Drawings

Figure 1 is a schematic diagram of a quasi-planar Ge waveguide and it's coupling to an IR detector;

Figure 2 is schematic of an optical arrangement used to observe broadband IR transmission or attenuation spectra through tapered quasi-planar Ge waveguide;

Figure 3A is a graph illustrating the transmission properties of the disclosed 20-µm-thick tapered waveguide;

Figure 3B is a graph illustrating a transmittance noise spectrum using the disclosed tapered waveguide;

Figure 3C is a graph illustrating the cutoff of transmission at 5100cm^{-1} using a prior art planar waveguide;

Figure 4A is a graph illustrating the attenuated total reflection (ATR) spectra of a liquid sample obtained with the disclosed tapered 20-μm-thick waveguide; and

Figure 4B is a graph illustrating the attenuated total reflection (ATR) spectra of a solid film sample obtained with the disclosed tapered 20-μm-thick waveguide.

Figure 5 is an alternate embodiment of the tapered waveguide;

Figure 6 is a graph illustrating the comparison spectra between acetone, rubber cement and Scotch® Tape using the waveguide of Figure 5;

Figure 7 illustrates the absorbance sensitivity of the waveguide of Figure 5 for three thickness;

Figure 8 is a graph of halorhodopsin spectra using the waveguide of Figure 5.

Detailed Description of the Invention

Thin, mid-IR-transmitting, waveguide sensors have now been designed and fabricated that overcome the prior art difficulties and provide an efficient means of coupling light. The crucial feature that permits high coupling efficiency of these waveguides is a gradual bi-directional taper. Tapering has been used for some years as a means of improving the optical throughput of small cylindrical waveguide sensors, e.g. glass optical fibers. Cylindrical fiber tapered wave guides can be produced by melting/softening and drawing, an approach that is not directly applicable to planar Ge waveguides. To produce a tapered thin planar waveguide is technically more difficult than tapering a cylindrical chalcogenide fiber, especially when the goal is to achieve a sensor thickness below 100 μm.

The melting/softening and drawing combination has been used for years to produce tapered shapes for waveguides as well as glass micropipettes, etc. The drawing process, when applied to a softened region of a piece of glass of arbitrary shape, tends to produce a taper that is more and more cylindrically symmetrical the longer the drawing is carried

out. There is no comparably simple process for generating a quasi-planar waveguide shape from a softened piece of glassy material.

The simplest procedure would be to roll a softened piece of glassy material against a hard surface. A tapered thickness is produced by this process, but with nowhere near the surface polish that is attainable for a drawn glass taper of cylindrical symmetry. An additional problem is that the resulting "waveguide" has irregular edges, which cause problems in the throughput. Ideally, a flat nearly planar waveguide should have linear, or perhaps smoothly curved, edges. Thus, it would appear that cylindrical fiber tapered waveguide concepts are not applicable to non-cylindrical, non-fiber waveguides.

The disclosed tapered, "quasi-planar," waveguides have properties that make them particularly useful for certain types of mid-IR evanescent-wave sensors. The term "quasi-planar" as employed herein, refers to a waveguide that has a single planar surface, and a secondary "quasi-planar" parallel surface. The quasi-planar surface deviates from a true planar surface in that it is an arcuate. This tapering improves the efficiency of the optical coupling both into the waveguide from an FTIR spectrometer, and out of the waveguide onto a small-area IR detector. The tapering further enables the elimination of an IR microscope to couple light through the waveguide. Instead, it is possible to obtain extremely efficient coupling with a detector directly coupled to an immersion lens. This optical arrangement enables the disclosed tapered waveguides to be useful as sensors, because it simplifies the positioning of optical accessories needed to couple light into the waveguide. Untapered waveguides require a microscope or other bulky focusing mirrors close to the waveguide, thereby blocking easy access to its surface for depositing materials to be analyzed. Additionally, the elimination of the IR microscope permits the sensors to be mounted horizontally, an added advantage when using liquids. Furthermore, using a Ge waveguide having a 20-μm$\times$1-mm cross section, sufficient throughput is obtained to give

signal/noise ratios in excess of 1,000 in over most of the 1000-5000 cm^{-1} range, with two (2) minutes of scanning at 8 cm^{-1} resolution. The small (0.02 mm^2) cross section of the waveguide yields great sensitivity to small numbers of IR-absorbing molecules near its surface. The optimum thickness for the waveguide is 1-μm, however due to the output obtained with the 20-μm waveguides, in many applications the increased output obtainable by1-μm will not provide any advantages.

The waveguides manufactured herein are from germanium prisms, however as the advantages over prior art waveguides are obtained through the science rather than the materials, other elements can be substituted. For example, silicon or cadmium tellurium, will behave similarly, although the mechanical properties of these, and other, materials will require attention to procedures. For example, CdTe is significantly more brittle than Ge and therefore requires additional care during the grinding procedures.

As illustrated in the schematic diagram 170 of Figure 1, the disclosed quasi-planar Ge waveguide 172 has been coupled to an IR detector 176, such as sold by Remspec Instruments, Sturbridge MA, model MOD-02. The focused input light 174, shown at left of the figure, is typically from an FTIR spectrometer. One of the flat surfaces of the waveguide 172 is first coated with a thin cladding layer of ZnS, or an equivalent coating, then cemented to a rigid substrate 178, such as quartz. The top, unadhered, surface of the waveguide 172 is ground to a large-radius arcuate shape having a cylindrical sector of radius ~300 mm. Preferably a commercial tool for grinding concave cylindrical lenses is used to grind and polish the waveguide, to enable the accurate tapering of the prism. When selecting a cladding layer or substrate, the physical properties in relation to one another and to the waveguide material must be taken into account. For example, when selecting a cladding material, the strength of attachment to the waveguide and to the cement/substrate must be considered. Selection of a substrate must take into consideration the rigidity,

optical transparency in the UV and the ability to reach a high degree of flatness in surface polish. The Ge/ZnS/quartz combination disclosed herein provides an example of the desirable material interaction and can be used as a baseline for comparison.

Although the end thickness, or apex, is not necessarily critical, the apex should be at least 4-fold thicker than the minimum thickness, or nadir, at the middle. The ends should also have a thickness no greater than the width of the waveguide for optimum optical performance using commercially available IR detector elements, which are square or circular. To obtain optimum performance, the waveguide end should be imaged onto the detector without any overhangs.

METHOD OF PREPARAITON

Tapered Ge waveguides are fabricated using modifications of previously published procedures, using a commercial tool for grinding the concave cylindrical lenses. Greater care is needed to avoid scratching the waveguide surface as it is more difficult to fix any scratch or gouge once it has occurred. This greater care includes a care in the selection and maintenance of grinding/polishing surfaces.

To make the tapered waveguides shown in Figure 1, custom polished 50×20×1 mm Ge prisms are used as the starting material. They are coated on one face with a 1.2-μm-thick CVD coating of ZnS and then cemented to 50×50×2-mm quartz substrates using a UV-curing optical adhesive. The substrate dimensions must be at least that of the prism to provide support, however, the dimensions beyond the periphery of the prism are determined by end use and convenience in handling. To form the tapered surface, the waveguides are ground using aluminum oxide grinding powders against a commercially available cylindrical grinding tool with an appropriate diameter. The coarser techniques are used until the tapered portion has almost reached the desired thickness. Pads, designed for use with curved surfaces, are used with the grinding tool and the powders to create the

grinding/polishing surface. The thickness of the middle can be determined by observing the interference pattern between reflections from the front and back surfaces of the Ge waveguide in an FTIR spectrum with an IR microscope in reflectance mode. At that point, the curved surface is polished with a slurry combination of aluminum oxide (12.5 μm) and diamond powder (0.1 μm) and particle embedded soft films. Careful fine polishing to a 0.1-μm, or below, finish is crucial for minimizing light scattering from imperfections in the surface. To accomplish the required finish, the films are covered with water during the polishing process with particle size within the embedded films decreasing with each polishing, i.e. 12.5, 9, 6, 3, 1, 0.5, 0.3 and 0.1-μm.

In the event the Ge prisms are not available at the desired end thickness, the prisms can be ground against a flat glass, or equivalent grinding stone, to the final thickness. The curved surface is then ground and polished as set forth above.

In Figure 2 collimated light output by a commercial FTIR spectrometer 182 with a blackbody source is focused along a horizontal optical axis, into the 1-mm^2 entrance aperture 190 of the vertically placed waveguide 186, by using a single off-axis paraboloid mirror 184 (f=25 mm). Alignment at the output end 192 of the waveguide 186 is greatly simplified by using a Remspec immersion detector 188, which has a short focal length IR-transmitting lens 194 directly in contact with the small- area HgCdTe detector 196. The output end 192 of the tapered waveguide 186 is placed as close as possible to the lens 194 and along its axis.

As illustrated in the graphs of the optical arrangement shown in Figures 3 and 4, broadband optical throughputs sufficient to saturate the Remspec detector/preamp combination 188 are easily achieved through a planar Ge waveguide of 20-μm thickness. Spectral measurements through this waveguide, measured with 8-cm^{-1} resolution over a

bandwidth of 0-7900 cm^{-1}, have a signal/noise ratio in excess of 1000 after only 2 min scan time (see fig. 3). This signal/noise ratio applies over the range 1000-2500 cm^{-1}.

However, there are some notable differences in the signal/noise ratio at sub-regions within the spectral range of 1000-2500 cm^{-1}. The relatively larger depletion of light at higher frequencies is due to greater scattering losses from imperfections at the surfaces of the thinner waveguide. Since all surface phenomena are magnified with a thinner waveguide, it is crucial to polish the tapered waveguide surface as thoroughly as possible.

The light spectrum transmitted through the 20-μm thick tapered waveguide, and graphed in Figure 3, is similar in most respects to that transmitted through flat Ge planar waveguides. The disclosed waveguide, however, increases the total amount of light transmitted through the waveguide, per unit cross-sectional area at the waveguide's thinnest point, by 4-5 fold greater than a planar waveguide.

The intensity spectrum from FTIR spectrometer with broadband blackbody IR source, shown in 3A, uses an HgCdTe detector, and reflects data gathered from the arrangement of Figures 1 and 2. In particular, the distinct cutoff of transmission near 5100 cm^{-1}, as illustrated in by the inset of Figure 3C, is characteristic of light transmitted through a prior-art planar Ge waveguide. The sharp attenuation bands near 2300 and 2000-1400 cm^{-1} are due to atmospheric CO_2 and H_2O vapor, respectively, in the open path of the IR beam. In 3B, 100% transmittance noise spectrum calculated from the ratio of two successive single-beam intensity spectra, each acquired in 2 min (1000 scans) with 8-cm^{-1} resolution is graphed. The tapered waveguide has a broad intrinsic absorption band near 3500 cm^{-1} that leads to substantial baseline irregularities in ratioed spectra (Fig. 3B). The peak-to-peak transmittance noise in the 2000-2200 cm^{-1} range is 0.1%. The peak-to-peak transmittance noise from the tapered waveguide is less than 0.2 as large as that measured in the same amount of time using a planar waveguide with a similar thickness.

The transmission spectrum of the tapered waveguide is especially unique for a feature that it lacks, namely the oscillatory interference pattern characteristic of planar waveguides with a fixed thickness and propagation angle. The observed oscillations in transmitted intensity arise from a fixed frequency separation between allowed waveguide modes. With the tapered waveguide, there is a wide range of propagation angles as well as a wide range of waveguide thicknesses. This results in a superposition of oscillation patterns continuously covering a wide range of different periods, i.e. no discernible oscillatory pattern at all.

Figure 4A shows the attenuated total reflection (ATR) spectra of a liquid while Figure 4B shows the ATR of a solid film sample. Both were obtained with a tapered 20-μm-thick waveguide and the light source and detector illustrated in Figures 1 and 2. The two samples shown are deuterated water (D_2O) and a thin film of halobacterial membrane containing lipid (25%) and protein (75%). In each case, the spectrum presented is $-\log(I/I_o)$, where I is the intensity spectrum measured in the presence of sample, and I_o is the spectrum measured in its absence. In each case the sample covered a region ~1 mm in area at the thinnest central region of the waveguide, the measurement time was 2 min (500 scans), and spectral resolution was 8 cm^{-1}.

The D_2O sample was measured with a 1-μL droplet covering only a ~1-mm length of the thinnest portion of the waveguide. Coverage of longer regions of the waveguide produced only small increases in the size of the absorbance bands. (Data not shown). The graph of Figure 4A shows a strong O-D stretch vibration near 2500 cm^{-1} and weaker D-O-D bending vibration near 1250 cm^{-1}.

The dried film of ~2 pmol bacteriorhodopsin (60 ng purple membrane) sample was prepared by drying a 1-μL droplet of a suspension of purple membrane fragments (50 μg/mL) onto the thinnest portion of the waveguide. As shown in 4B, the three (3)

strongest bands near 1650, 1550, and 1200 cm^{-1} are due to amide I, amide II, and amide III vibrations, respectively, and are characteristic of the peptide backbone.

In comparison to prior art spectra of similar samples obtained using an IR microscope with planar waveguides 30-50 μm in thickness, the spectra of Figure 4 have substantially improved signal-noise ratios for 10-20× shorter measurement times. For example, the noise level in both of the spectra of Figure 4 (obtained with 500 scans each) is 0.001 absorbance units, whereas in spectra obtained with the microscope-coupled planar waveguides, the noise level was typically 0.01 absorbance units for 10,000 or 20,000 scans.

At the same time, the absorbance signals are somewhat reduced (between 3- and 5-fold) for similar sized samples on the tapered 20-μm waveguide, as opposed to the untapered 30-μm waveguides with 45° bevels used previously in the prior art. The reduction in attenuation signals is due to the predominance in the tapered waveguide of light propagating at relatively low off-axis angles, i.e. angles that lie less than 45° away from the waveguide surface plane. Light in such modes is absorbed relatively inefficiently by molecules at the surface, giving rise to smaller attenuation signals per molecule.

The principal advantage of tapering thin Ge planar waveguides is to permit a substantial increase in throughput for a given sensor thickness, making it possible to detect the IR signal level more precisely in a shorter length of time. The increase in throughput results from filling the large numerical aperture of a high-index waveguide medium (Ge, n=4). With an untapered planar waveguide, the largest numerical aperture that can be attained inside the waveguide is equal to the numerical aperture of the element that focuses light through air onto the end of the waveguide.

On the other hand, the largest numerical aperture that can be propagated through a tapered waveguide is determined by the refractive index of the waveguide material and it's

cladding, and is equal to $(n_1^2-n_2^2)^{1/2}$. Here n_1 is the refractive index of the waveguide medium (n_1=4 for Ge), while n_2 is the highest refractive index of the cladding materials in contact with the waveguide (n_2 = 2.26 for ZnS). For our ZnS-clad Ge waveguide, this maximum numerical aperture is 3.3. Thus, ~4-fold more light energy can be propagated through the sensing region of a planar Ge waveguide than can be obtained by focusing light through air into the (untapered) waveguide edge.

Gradually tapering a waveguide enables an increase in the numerical aperture. In such a taper, the product of the numerical aperture and waveguide thickness remains constant, as long as the maximum numerical aperture of the waveguide is not exceeded. A cone of light with numerical aperture of 0.3 that is transmitted into a 1-mm thick Ge waveguide maintains that numerical aperture across the air/Ge interface. Inside the Ge, it has a half- angular spread of only arcsine (0.3/4)=4°. It is possible to achieve a numerical aperture of 3.3 by gradually tapering the waveguide by a factor of about10. That is, once a waveguide thickness of about100 μm is reached, the numerical aperture of the waveguide is filled. At this thickness, the cone of propagating light rays extends all the way to the critical angle between Ge and ZnS, that is, to a half-angular spread of arcos (2.26/4)=56° .

The taper factor used herein (1 mm/20 μm=50) is much larger than the ratio of the maximum numerical aperture of the waveguide (3.3) to the numerical aperture of the input focusing optic (~0.3). This excess taper factor is intended to guarantee that, to the greatest extent possible, the numerical aperture of the sensing region of the waveguide is filled. With the particular light source present in the Midac spectrometer used herein, it is not difficult to fill the 1×1 mm input aperture of the tapered waveguide. Thus, a significant fraction of the input light is expected to be coupled out of the waveguide, i.e. to exceed the critical angle, as the waveguide is tapered down to its minimum thickness. It should be noted that the optimum apex to nadir ratio is dependent upon the detector size and shape

and, when taken in conjunction with the teachings herein, will be apparent to those skilled in the art.

Much of the light that goes into one end of the waveguide is lost as it travels into the middle (thinnest) portion of the waveguide, but then as the light travels into the region where the waveguide tapers outward again, there is no further loss of light energy (or flux). The loss of light is therefore not due simply to the presence of non-parallel surfaces; but more specifically to the presence of surfaces that converge to a thickness less than 1/4 of the input thickness. That is, nearly all the light present in the tapered region reaches the output face of the waveguide.

From here, the light is efficiently focused onto the 100-μm×100 μm area of the HgCdTe element in the Remspec detector. The use of an immersion lens in this detector provides an efficient coupling method that is extremely insensitive to the position of the fiber (or waveguide) output end. This greatly simplifies waveguide alignment, relative to the procedures that were required previously with a microscope. When incorporating a microscope, the output end of the waveguide had to be positioned at the very small focal area of the microscope's objective since the IR signal could be lost entirely with a mispositioning of as little as 50 μm.

The 1-mm width of the waveguide used in the example herein was chosen as the minimum width that could be easily manipulated without breaking. The thickness at the ends in these examples is the same as the width to match the square shape of the IR detector element used in the testing. The prism was then tapered as stated heretofore. Various taper ratios were tested with the result that the greater the thickness, the lower the sensitivity. A minimum 0.1-mm thickness, which corresponds to a taper ratio of 10, gave a high light throughput, but a lower (at least 5-fold) sensitivity to analyte at the surface

than the 20μm thickness. Test data (not shown) showed a continuous increase in sensitivity as the thickness of the waveguide decreased.

The wide range of propagation angles present at the sensing area of the tapered quasi-planar waveguide eliminates the distracting oscillatory transmission pattern that is observed for thin planar Ge waveguides. This is advantageous for a sensor, because it means that there are no sharp features in the spectrum that could be mistaken for absorption bands of a material present at the waveguide surface. Furthermore, the transmitted intensity at any frequency is not nearly as sensitive to waveguide alignment as with true planar waveguides.

The wide range of propagation angles present can lead to some degree of non-linearity of the absorbance signal, presenting small deviations from logarithmic response (i.e. the absorbance nonlinearities). In particular, the nonlinear response is not important for measurement of different spectra of samples that are subjected to an in situ perturbation while they are adsorbed or adhered to the surface of the waveguide. Additionally, the nonlinear response can be unimportant if there is a single known analyte, and a calibration curve can be established.

With the tapered waveguide, most of the internal reflections occur within a fairly small region near the point of minimum thickness. Thus, molecules located at the surface of this region predominate in the attenuation spectrum. This is a particular advantage for obtaining ATR spectra of small samples that must be kept submerged under water, e.g. biological samples. A relatively large pool of aqueous buffer can cover the surface of the entire waveguide and its supporting quartz substrate. Even when the entire waveguide is covered, this produces only about as much background attenuation as is shown in Figure 4A, i.e. maximally 0.2-0.3 absorbance units. Meanwhile, a biological sample that covers

only the ~1 mm^2 area above the thinnest portion of the waveguide can be detected and analyzed with great sensitivity.

The disclosed coupling method enables measurement of ATR-IR spectra using <100-μm thick planar waveguides in a horizontal configuration. The 20 μm thick waveguide affords high attenuation values for a small number of IR- absorbing molecules at the waveguide surface. This, and the improvement in signal/noise ratio obtained as a result of the coupling efficiency, make tapered Ge waveguides particularly well suited for measuring spectra of small biological samples, such as the detection of different spectra from various components of the cell membranes of individual frog eggs, 1.5 mm in diameter, that must be submerged under a bulk aqueous buffer.

The quasi-tapered waveguide 200 illustrated in Figure 5 is tapered as set forth above. The arcuate surface of the Ge prism 202 is then coated with a ZnS coating 204 and embedded into an epoxide substrate 208.

In Figure 6 the graphed spectra illustrates the comparison between Scotch® Tape, rubber cement and acetone. The spectra were read using the waveguide 200 having a 12 μm waveguide nadir. As can be seen in the graph, the Scotch® Tape 300 and the rubber cement 302 have similar spectra, showing that the tape is invisible and that the only material readable is the adhesive. The acetone spectrum 304 , however, provides a completely different spectrum reading than the two adhesives.

In Figure 7 the absorbance spectrum of D_2O, using the waveguide arrangement of Figure 5, is compared at different waveguide thickness. As illustrated, the sensitivity of the waveguide increased dramatically when using a 12μm waveguide. The overall sensitivity increase is substantially greater than the increase between the 70μm and 30μm readings.

Figure 9 illustrates the spectra of halorhodopsin using the 12μm waveguide of Figure 5.

What is claimed is:

1. A quasi-planar waveguide, said waveguide having a first surface, a second surface and a perimeter, said first surface having an arcuate contour and said second surface being planar, at least one of said first surface and said second surface being coated with a cladding, wherein said first surface is concave relative to said second surface.
2. The waveguide of claim 1 wherein said first surface and said second surface are substantially parallel.
3. The waveguide of claim 1 wherein said perimeter is comprised of multiple opposing planar surfaces, said perimeter surfaces being at right angles to said second surface.
4. The waveguide of claim 1 wherein said clad surface is adhered to a substrate, said substrate having a perimeter at least equal to said waveguide perimeter and having a thickness sufficient to support said waveguide.
5. The waveguide of claim 1 wherein said waveguide is made from single-crystal germanium.
6. The waveguide of claim 1 wherein said arcuate surface has an apex at least about four times greater than said surface nadir.
7. The waveguide of claim 1 wherein said waveguide is coupled directly to an IR detector.
8. The waveguide of claim 7 wherein said waveguide is mounted horizontally.
9. The waveguide of claim 1 wherein said waveguide has a nadir of less than 100μm.
10. The waveguide of claim 9 wherein said waveguide has a nadir of less than 20μm.
11. The waveguide of claim 10 wherein said waveguide has a nadir of about 1μm.
12. The waveguide of claim 1 wherein said cladding is ZnS.
13. The waveguide of claim 1 wherein said arcuate surface is polished to about a 0.1 μm finish.

14. The waveguide of claim 1 wherein said arcuate surface has a ratio of nadir to apex taper of at least about10.

15. The waveguide of claim 14 wherein said arcuate surface has a ratio of nadir to apex taper of up to about 50.

16. A quasi-planar waveguide, said waveguide being a single-crystal germanium, said waveguide being coupled directly to an IR detector and having:

a. a first surface, said first surface having an arcuate surface with an apex about four times thicker than said surface's nadir, said arcuate surface having a taper of about10

b. a second surface, said second surface being coated with a cladding and adhered to a substrate, said substrate having a perimeter at least equal to said waveguide perimeter and having a thickness sufficient to support said waveguide

c. a perimeter, said perimeter being comprised of multiple opposing planar surfaces, said perimeter surfaces being at right angles to said second surface

wherein said waveguide increases IR signal throughput by filling the large numerical aperture thereby increasing the aperture to at least 1.

17. The method of producing a quasi-planar waveguide having a first surface, a second surface and a perimeter form of multiple opposing planar surfaces at right angles to said second surface, comprising the steps of:

a. coating said second surface with a cladding;

b. adhering said second surface to a substrate having a perimeter at least equal to said waveguide perimeter and a thickness sufficient to support said waveguide;

c. grinding said first surface to a width proximate said nadir;

d. minimizing light scattering by polishing said first surface to about a 0.1 μm

e. coupling directly to an IR detector

f. passing light from a light source, through said waveguide, to said IR detector;

wherein said waveguide increases IR signal throughput by about 4 fold by filling the large numerical aperture thereby increasing the aperture to at least 1.

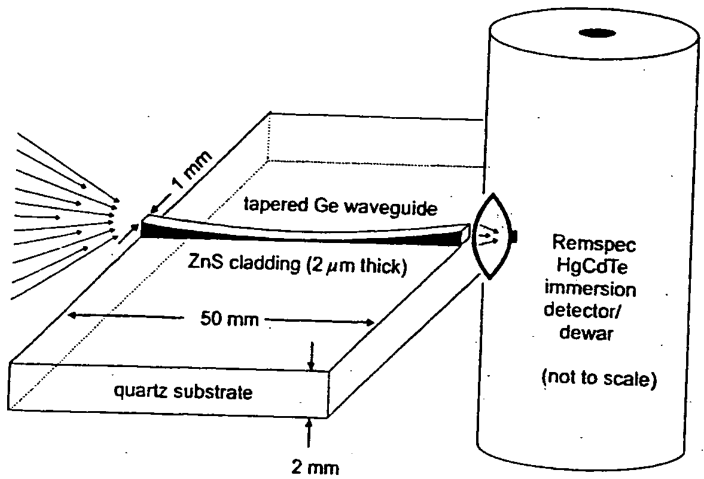
1 mm
tapered Ge waveguide
ZnS cladding (2 μm thick)
50 mm
quartz substrate
2 mm
Remspec
HgCdTe
immersion
detector/
dewar
(not to scale)

Fig. 1

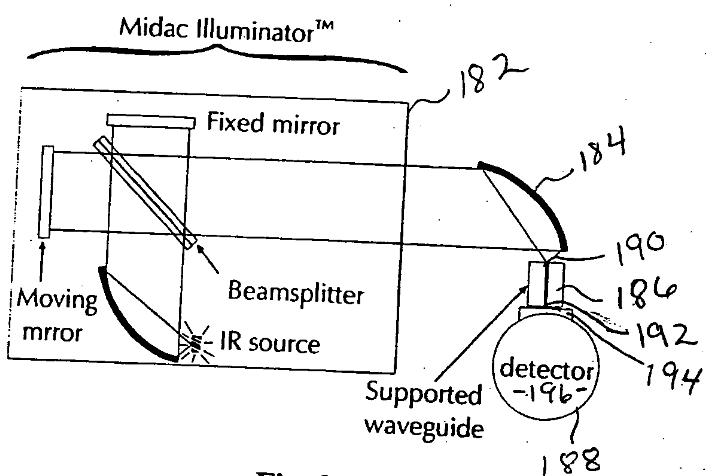
Midac Illuminator™
182
Fixed mirror
184
190
186
192
194
Moving
mrror
Beamsplitter
IR source
detector
-196-
Supported
waveguide
188

Fig. 2

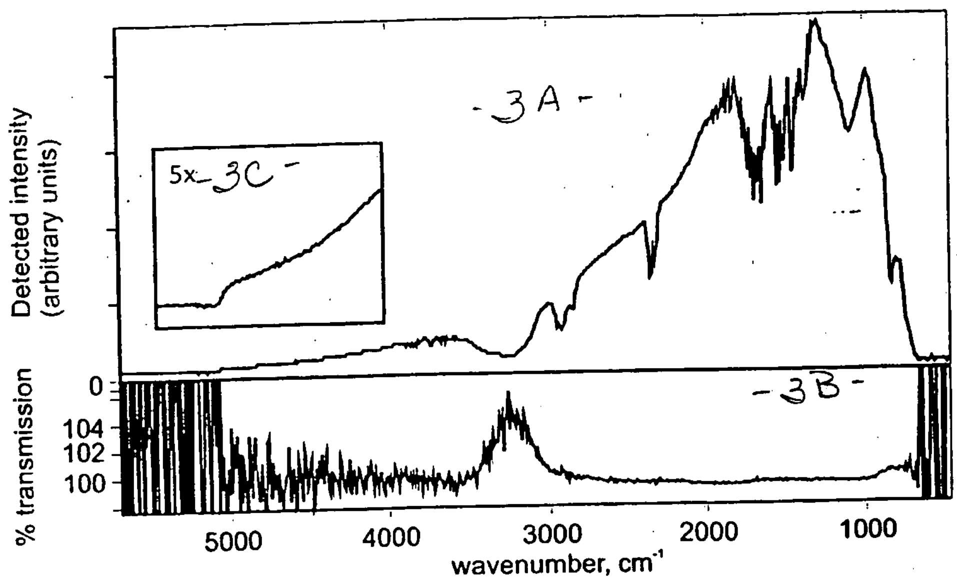

Fig. 3

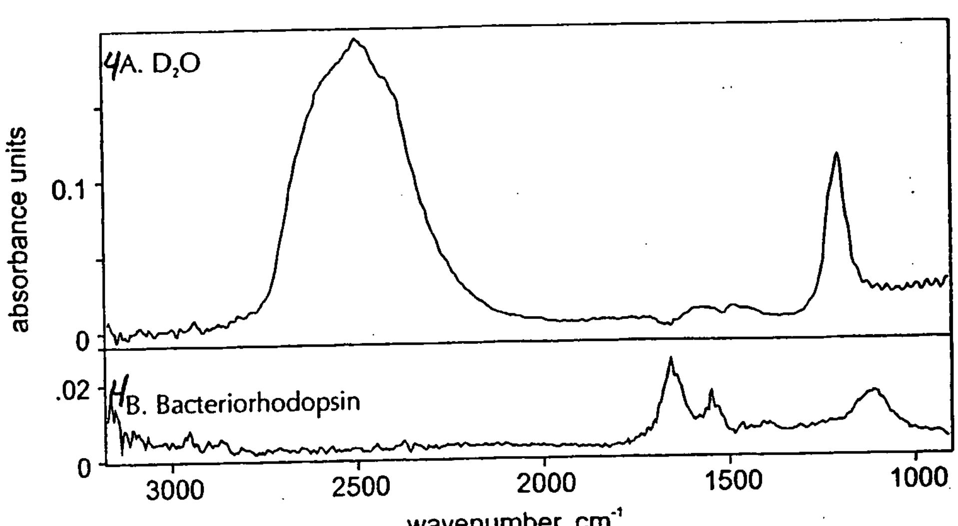

Fig. 4

PCT

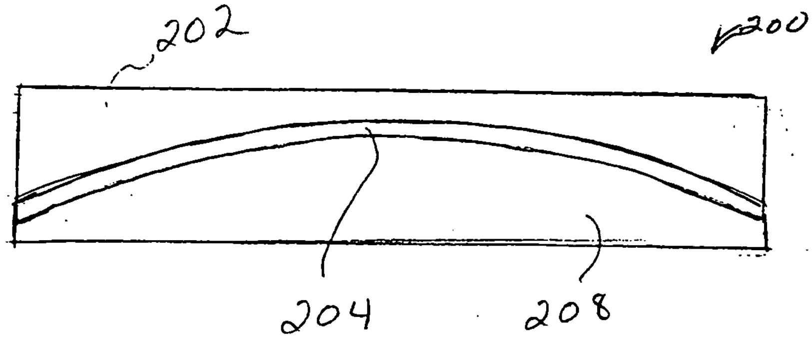
202
200
204
208

Fig 5

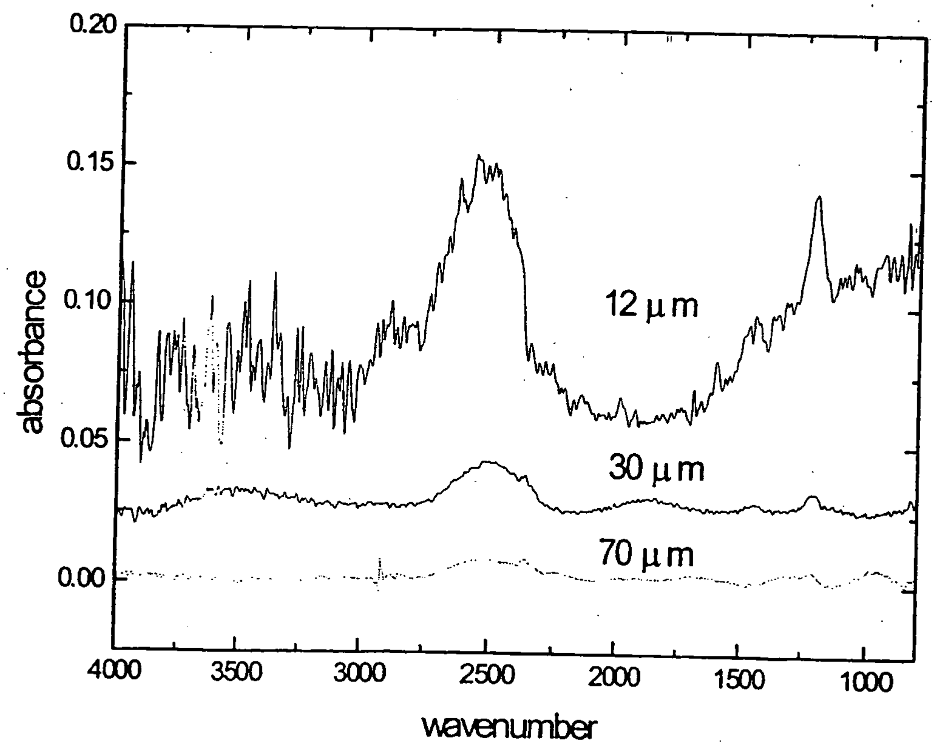
0.20
0.15
0.10
0.05
0.00
absorbance
12 μm
30 μm
70 μm
4000
3500
3000
2500
2000
1500
1000
wavenumber

Fig 7

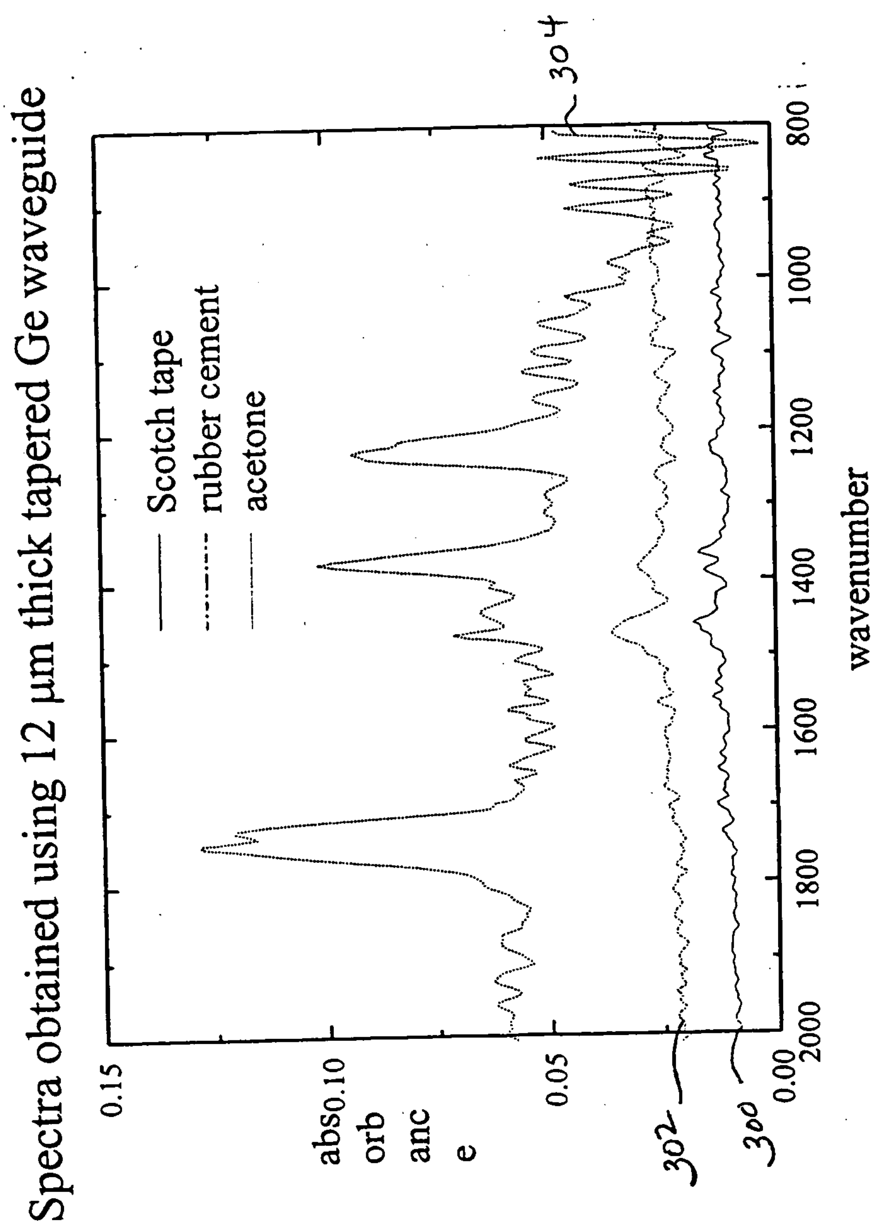
Spectra obtained using 12 μm thick tapered Ge waveguide
Scotch tape
rubber cement
acetone
absorbance
wavenumber
0.15
0.10
0.05
0.00
2000
1800
1600
1400
1200
1000
800
300
302
304

Fig 6

Spectra of halorhodopsin obtained using 12 μm thick tapered Ge waveguide

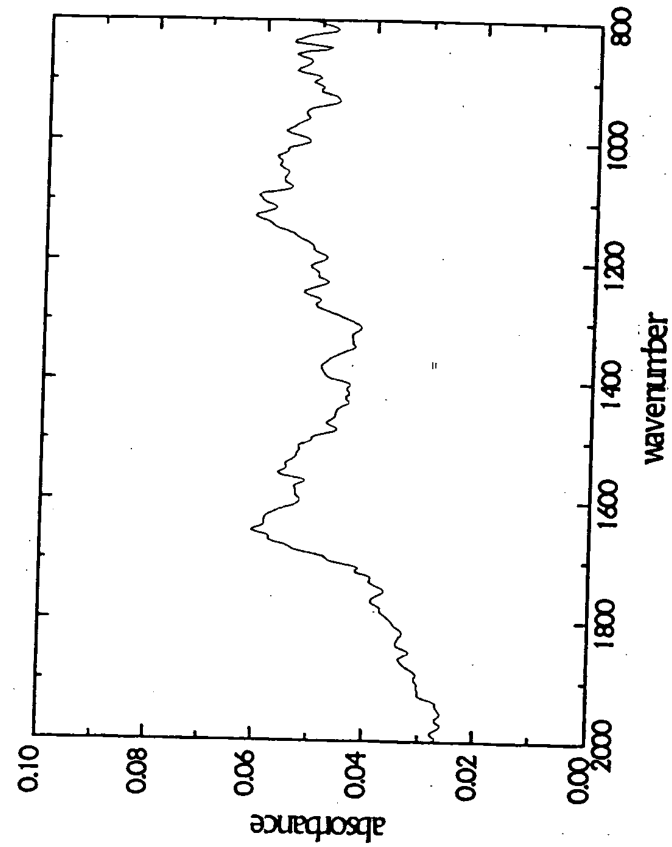

Fig 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/24974

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :GO2B 6/10; GOIN 21/00
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,980,831A (BRAIMAN ET AL.) 09 NOVEMBER. 1999 (09.11.99), SEE FIGURE 1 AND ENTIRE DOCUMENT	1-17
A	US 5,949,942 A (O'Connor) 07 SEPTEMBER 1999 (07.09.99) SEE FIG. 1, AND ENTIRE DOCUMENT	1-17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 31 JANUARY 2000	Date of mailing of the international search report 16 FEB 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 308-7724	Authorized officer PHAN T. H. PALMER Telephone No. (703) 308-4848

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/24974

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

385/129, 12, 23
422/82.11

B. FIELDS SEARCHED
Minimum documentation searched
Classification System: U.S.

385/129, 12, 123, 130-132, 147
422/82.11
250/339.12

CORRECTED VERSION*

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : G02B 6/10, G01N 21/00

A1

(11) International Publication Number: WO 00/36442

(43) International Publication Date: 22 June 2000 (22.06.00)

(21) International Application Number: PCT/US99/24974

(22) International Filing Date: 25 October 1999 (25.10.99)

(30) Priority Data:
60/106,132 29 October 1998 (29.10.98) US

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(74) Agent: PARKER, Sheldon, H.; Parker & De Stefano, P.C., Suite 300, 300 Preston Avenue, Charlottesville, VA 22902 (US).

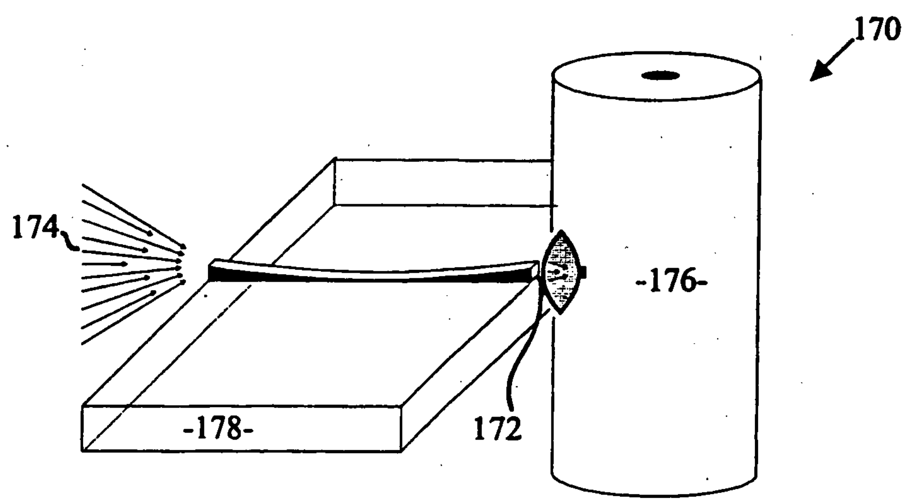
(81) Designated States: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: TAPERED QUASI-PLANAR GERMANIUM WAVEGUIDES FOR MID-IR SENSING

(57) Abstract

A quasi-planar waveguide for transmission of mid-IR sensing is disclosed. The Ge waveguide (172) is tapered from a thichness of 1mm at the ends to a minimum of 20–100 μ at the center. This tapering improves the efficiency of the optical coupling both into the waveguide from an FTIR spectrometer, and out of the waveguide onto a small-area IR detector (176). The tapering makes it possible to dispense with using an IR microscope couple light through the waveguide (172), enabling efficient coupling with a detector (176) directly coupled to an immersion lens. This optical arrangement makes such thin supported waveguides more useful as sensors, because they can be made quite long (e.g. 50 mm) and mounted horizontally. Furthermore, even with a 20-μ x 1-mm cross section, sufficient throughput is obtained to give signal/noise ratios in excess of 1000 over most of the 1000–5000 cm range, with just 2 min of scanning at 8 cm resolution. The small (0.02 mm) cross section of the waveguide (172) nevertheless yields great sensitivity to small numbers of IR-absorbing molecules near its surface.



*(Referred to in PCT Gazette No. 44/2000, Section II)

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TAPERED QUASI-PLANAR GERMANIUM WAVEGUIDES FOR MID-IR SENSING

This work was supported by NSF grant MCB-9722887 to Mark S. Braiman.

Cross-reference to Related Patent Applications

The present application claims the benefits under 35 U.S.C. 119(e) of provisional patent application serial number 60/106,132, filed October 29, 1998. This application incorporates by reference, as though recited in full, the disclosure of parent application 08/874,711 and copending provisional patent application serial number 60/106,132.

Background of the Invention

Supported planar IR waveguides, having a thickness between 50-100 μm, have been fabricated by grinding and polishing single crystals of germanium. These thin planar Ge waveguides are useful as mid-IR evanescent-wave sensors. A significant portion of the light energy transmitted through such waveguides actually propagates outside the germanium, as an evanescent wave in the surrounding medium. With <100-μm-thick waveguides, a very small number of IR- absorbing molecules near the surface of the waveguide can significantly attenuate the light transmitted through the waveguide, allowing the measurement of an ATR (attenuated total reflection) spectrum. Sizable ATR bands are therefore observed from thin surface layers under 1 mm^2 in area. This includes thin coatings on small pieces of polymer film, as well as patches of the plasma membrane of large individual cells, e.g. frog oocytes.

One difficulty with using thin planar Ge waveguides as internal reflection elements (IREs) is coupling measurable amounts of light through such waveguides and onto a detector. Prior art requires the use of an IR microscope in order to measure useful spectra through waveguides having a thickness between 30-100 μm. Use of a microscope, however, results in significant limitations on the waveguide configurations that can be

used. In particular, waveguide lengths were generally limited to ~12 mm, the maximum separation between objective and condenser focal points on commercial FTIR microscopes. Furthermore, the waveguides had to be positioned vertically, i.e. along the optical axis of the microscope. This is an inconvenience for samples containing liquids, especially small biological samples.

Summary of the Invention

A quasi-planar waveguide, preferable made from single-crystal germanium, is disclosed wherein one of the surfaces has an arcuate contour while a parallel, second surface is planar, the first surface being concave relative to the second surface. The perimeter is comprised of multiple opposing planar surfaces at right angles to the second surface. The second surface is coated with a cladding, such as ZnS and then adhered to a substrate, such as quartz. The substrate must have a perimeter at least equal to that of the waveguide and a thickness sufficient to support the waveguide.

The arcuate surface of the waveguide has an apex at least about four times greater than the nadir, with a preferred ratio of nadir to apex taper of at least about 10 and up to about 50. The nadir of the waveguide is less than 100μm, and preferably in the range of 1 to 20μm. The arcuate surface is polished to about a 0.1 μm finish to prevent light scattering.

The tapered waveguide can be coupled directly to an IR detector, eliminating the need for a microscope and enabling more accurate alignment. The elimination of the microscope also enables the waveguide to be mounted horizontally. The tapered waveguide increases IR signal throughput by about 4-5 fold, a result of filling the large numerical aperture of a high-index waveguide medium (Ge, n=4). This increase, for a given sensor thickness, makes it possible to detect the IR signal level more precisely in a shorter length of time. With an untapered planar waveguide, the largest numerical aperture

that can be attained inside the waveguide is equal to the numerical aperture of the element that focuses light through air onto the end of the waveguide. This must always be less than 1, and for commercially available focusing optics is typically 0.5-0.8.

On the other hand, the fundamental limitation on the largest numerical aperture that can be propagated inside a dielectric waveguide is the refractive index of the waveguide material and it's cladding, and is equal to $(n_1^2-n_2^2)^{1/2}$. Here n_1 is the refractive index of the waveguide medium (n_1=4 for Ge), while n_2 is the highest refractive index of the cladding materials in contact with the waveguide (n_2 = 2.26 for ZnS). For the disclosed ZnS-clad Ge waveguide, this maximum numerical aperture is 3.3, or approximately 4-fold higher than the numerical aperture of available focusing optics. In theory, at least ~4-fold more light energy can be propagated through the sensing region of a planar Ge waveguide than can be obtained by focusing light through air into the edge of an untapered waveguide of the same minimum thickness. This theoretical maximum throughput is, in fact, closely approached with the tapered waveguide design.

Brief Description of the Drawings

Figure 1 is a schematic diagram of a quasi-planar Ge waveguide and it's coupling to an IR detector;

Figure 2 is schematic of an optical arrangement used to observe broadband IR transmission or attenuation spectra through tapered quasi-planar Ge waveguide;

Figure 3A is a graph illustrating the transmission properties of the disclosed 20-μm-thick tapered waveguide;

Figure 3B is a graph illustrating a transmittance noise spectrum using the disclosed tapered waveguide;

Figure 3C is a graph illustrating the cutoff of transmission at 5100cm^{-1} using a prior art planar waveguide;

Figure 4A is a graph illustrating the attenuated total reflection (ATR) spectra of a liquid sample obtained with the disclosed tapered 20-μm-thick waveguide; and

Figure 4B is a graph illustrating the attenuated total reflection (ATR) spectra of a solid film sample obtained with the disclosed tapered 20-μm-thick waveguide.

Figure 5 is an alternate embodiment of the tapered waveguide;

Figure 6 is a graph illustrating the comparison spectra between acetone, rubber cement and Scotch® Tape using the waveguide of Figure 5;

Figure 7 illustrates the absorbance sensitivity of the waveguide of Figure 5 for three thickness;

Figure 8 is a graph of halorhodopsin spectra using the waveguide of Figure 5.

Detailed Description of the Invention

Thin, mid-IR-transmitting, waveguide sensors have now been designed and fabricated that overcome the prior art difficulties and provide an efficient means of coupling light. The crucial feature that permits high coupling efficiency of these waveguides is a gradual bi-directional taper. Tapering has been used for some years as a means of improving the optical throughput of small cylindrical waveguide sensors, e.g. glass optical fibers. Cylindrical fiber tapered wave guides can be produced by melting/softening and drawing, an approach that is not directly applicable to planar Ge waveguides. To produce a tapered thin planar waveguide is technically more difficult than tapering a cylindrical chalcogenide fiber, especially when the goal is to achieve a sensor thickness below 100 μm.

The melting/softening and drawing combination has been used for years to produce tapered shapes for waveguides as well as glass micropipettes, etc. The drawing process, when applied to a softened region of a piece of glass of arbitrary shape, tends to produce a taper that is more and more cylindrically symmetrical the longer the drawing is carried

out. There is no comparably simple process for generating a quasi-planar waveguide shape from a softened piece of glassy material.

The simplest procedure would be to roll a softened piece of glassy material against a hard surface. A tapered thickness is produced by this process, but with nowhere near the surface polish that is attainable for a drawn glass taper of cylindrical symmetry. An additional problem is that the resulting "waveguide" has irregular edges, which cause problems in the throughput. Ideally, a flat nearly planar waveguide should have linear, or perhaps smoothly curved, edges. Thus, it would appear that cylindrical fiber tapered waveguide concepts are not applicable to non-cylindrical, non-fiber waveguides.

The disclosed tapered, "quasi-planar," waveguides have properties that make them particularly useful for certain types of mid-IR evanescent-wave sensors. The term "quasi-planar" as employed herein, refers to a waveguide that has a single planar surface, and a secondary "quasi-planar" parallel surface. The quasi-planar surface deviates from a true planar surface in that it is an arcuate. This tapering improves the efficiency of the optical coupling both into the waveguide from an FTIR spectrometer, and out of the waveguide onto a small-area IR detector. The tapering further enables the elimination of an IR microscope to couple light through the waveguide. Instead, it is possible to obtain extremely efficient coupling with a detector directly coupled to an immersion lens. This optical arrangement enables the disclosed tapered waveguides to be useful as sensors, because it simplifies the positioning of optical accessories needed to couple light into the waveguide. Untapered waveguides require a microscope or other bulky focusing mirrors close to the waveguide, thereby blocking easy access to its surface for depositing materials to be analyzed. Additionally, the elimination of the IR microscope permits the sensors to be mounted horizontally, an added advantage when using liquids. Furthermore, using a Ge waveguide having a 20-μm×1-mm cross section, sufficient throughput is obtained to give

signal/noise ratios in excess of 1,000 in over most of the 1000-5000 cm^{-1} range, with two (2) minutes of scanning at 8 cm^{-1} resolution. The small (0.02 mm^2) cross section of the waveguide yields great sensitivity to small numbers of IR-absorbing molecules near its surface. The optimum thickness for the waveguide is 1-μm, however due to the output obtained with the 20-μm waveguides, in many applications the increased output obtainable by1-μm will not provide any advantages.

The waveguides manufactured herein are from germanium prisms, however as the advantages over prior art waveguides are obtained through the science rather than the materials, other elements can be substituted. For example, silicon or cadmium tellurium, will behave similarly, although the mechanical properties of these, and other, materials will require attention to procedures. For example, CdTe is significantly more brittle than Ge and therefore requires additional care during the grinding procedures.

As illustrated in the schematic diagram 170 of Figure 1, the disclosed quasi-planar Ge waveguide 172 has been coupled to an IR detector 176, such as sold by Remspec Instruments, Sturbridge MA, model MOD-02. The focused input light 174, shown at left of the figure, is typically from an FTIR spectrometer. One of the flat surfaces of the waveguide 172 is first coated with a thin cladding layer of ZnS, or an equivalent coating, then cemented to a rigid substrate 178, such as quartz. The top, unadhered, surface of the waveguide 172 is ground to a large-radius arcuate shape having a cylindrical sector of radius ~300 mm. Preferably a commercial tool for grinding concave cylindrical lenses is used to grind and polish the waveguide, to enable the accurate tapering of the prism. When selecting a cladding layer or substrate, the physical properties in relation to one another and to the waveguide material must be taken into account. For example, when selecting a cladding material, the strength of attachment to the waveguide and to the cement/substrate must be considered. Selection of a substrate must take into consideration the rigidity,

optical transparency in the UV and the ability to reach a high degree of flatness in surface polish. The Ge/ZnS/quartz combination disclosed herein provides an example of the desirable material interaction and can be used as a baseline for comparison.

Although the end thickness, or apex, is not necessarily critical, the apex should be at least 4-fold thicker than the minimum thickness, or nadir, at the middle. The ends should also have a thickness no greater than the width of the waveguide for optimum optical performance using commercially available IR detector elements, which are square or circular. To obtain optimum performance, the waveguide end should be imaged onto the detector without any overhangs.

METHOD OF PREPARAITON

Tapered Ge waveguides are fabricated using modifications of previously published procedures, using a commercial tool for grinding the concave cylindrical lenses. Greater care is needed to avoid scratching the waveguide surface as it is more difficult to fix any scratch or gouge once it has occurred. This greater care includes a care in the selection and maintenance of grinding/polishing surfaces.

To make the tapered waveguides shown in Figure 1, custom polished 50×20×1 mm Ge prisms are used as the starting material. They are coated on one face with a 1.2-μm-thick CVD coating of ZnS and then cemented to 50×50×2-mm quartz substrates using a UV-curing optical adhesive. The substrate dimensions must be at least that of the prism to provide support, however, the dimensions beyond the periphery of the prism are determined by end use and convenience in handling. To form the tapered surface, the waveguides are ground using aluminum oxide grinding powders against a commercially available cylindrical grinding tool with an appropriate diameter. The coarser techniques are used until the tapered portion has almost reached the desired thickness. Pads, designed for use with curved surfaces, are used with the grinding tool and the powders to create the

grinding/polishing surface. The thickness of the middle can be determined by observing the interference pattern between reflections from the front and back surfaces of the Ge waveguide in an FTIR spectrum with an IR microscope in reflectance mode. At that point, the curved surface is polished with a slurry combination of aluminum oxide (12.5 μm) and diamond powder (0.1 μm) and particle embedded soft films. Careful fine polishing to a 0.1-μm, or below, finish is crucial for minimizing light scattering from imperfections in the surface. To accomplish the required finish, the films are covered with water during the polishing process with particle size within the embedded films decreasing with each polishing, i.e. 12.5, 9, 6, 3, 1, 0.5, 0.3 and 0.1-μm.

In the event the Ge prisms are not available at the desired end thickness, the prisms can be ground against a flat glass, or equivalent grinding stone, to the final thickness. The curved surface is then ground and polished as set forth above.

In Figure 2 collimated light output by a commercial FTIR spectrometer 182 with a blackbody source is focused along a horizontal optical axis, into the 1-mm^2 entrance aperture 190 of the vertically placed waveguide 186, by using a single off-axis paraboloid mirror 184 (f=25 mm). Alignment at the output end 192 of the waveguide 186 is greatly simplified by using a Remspec immersion detector 188, which has a short focal length IR-transmitting lens 194 directly in contact with the small- area HgCdTe detector 196. The output end 192 of the tapered waveguide 186 is placed as close as possible to the lens 194 and along its axis.

As illustrated in the graphs of the optical arrangement shown in Figures 3 and 4, broadband optical throughputs sufficient to saturate the Remspec detector/preamp combination 188 are easily achieved through a planar Ge waveguide of 20-μm thickness. Spectral measurements through this waveguide, measured with 8-cm^{-1} resolution over a

bandwidth of 0-7900 cm^{-1}, have a signal/noise ratio in excess of 1000 after only 2 min scan time (see fig. 3). This signal/noise ratio applies over the range 1000-2500 cm^{-1}.

However, there are some notable differences in the signal/noise ratio at sub-regions within the spectral range of 1000-2500 cm^{-1}. The relatively larger depletion of light at higher frequencies is due to greater scattering losses from imperfections at the surfaces of the thinner waveguide. Since all surface phenomena are magnified with a thinner waveguide, it is crucial to polish the tapered waveguide surface as thoroughly as possible.

The light spectrum transmitted through the 20-μm thick tapered waveguide, and graphed in Figure 3, is similar in most respects to that transmitted through flat Ge planar waveguides. The disclosed waveguide, however, increases the total amount of light transmitted through the waveguide, per unit cross-sectional area at the waveguide's thinnest point, by 4-5 fold greater than a planar waveguide.

The intensity spectrum from FTIR spectrometer with broadband blackbody IR source, shown in 3A, uses an HgCdTe detector, and reflects data gathered from the arrangement of Figures 1 and 2. In particular, the distinct cutoff of transmission near 5100 cm^{-1}, as illustrated in by the inset of Figure 3C, is characteristic of light transmitted through a prior-art planar Ge waveguide. The sharp attenuation bands near 2300 and 2000-1400 cm^{-1} are due to atmospheric CO_2 and H_2O vapor, respectively, in the open path of the IR beam. In 3B, 100% transmittance noise spectrum calculated from the ratio of two successive single-beam intensity spectra, each acquired in 2 min (1000 scans) with 8-cm^{-1} resolution is graphed. The tapered waveguide has a broad intrinsic absorption band near 3500 cm^{-1} that leads to substantial baseline irregularities in ratioed spectra (Fig. 3B). The peak-to-peak transmittance noise in the 2000-2200 cm^{-1} range is 0.1%. The peak-to-peak transmittance noise from the tapered waveguide is less than 0.2 as large as that measured in the same amount of time using a planar waveguide with a similar thickness.

The transmission spectrum of the tapered waveguide is especially unique for a feature that it lacks, namely the oscillatory interference pattern characteristic of planar waveguides with a fixed thickness and propagation angle. The observed oscillations in transmitted intensity arise from a fixed frequency separation between allowed waveguide modes. With the tapered waveguide, there is a wide range of propagation angles as well as a wide range of waveguide thicknesses. This results in a superposition of oscillation patterns continuously covering a wide range of different periods, i.e. no discernible oscillatory pattern at all.

Figure 4A shows the attenuated total reflection (ATR) spectra of a liquid while Figure 4B shows the ATR of a solid film sample. Both were obtained with a tapered 20-μm-thick waveguide and the light source and detector illustrated in Figures 1 and 2 . The two samples shown are deuterated water (D_2O) and a thin film of halobacterial membrane containing lipid (25%) and protein (75%). In each case, the spectrum presented is –log(I/I_o), where I is the intensity spectrum measured in the presence of sample, and I_o is the spectrum measured in its absence. In each case the sample covered a region ~1 mm in area at the thinnest central region of the waveguide, the measurement time was 2 min (500 scans), and spectral resolution was 8 cm^{-1}.

The D_2O sample was measured with a 1-μL droplet covering only a ~1-mm length of the thinnest portion of the waveguide. Coverage of longer regions of the waveguide produced only small increases in the size of the absorbance bands. (Data not shown). The graph of Figure 4A shows a strong O-D stretch vibration near 2500 cm^{-1} and weaker D-O-D bending vibration near 1250 cm^{-1}.

The dried film of ~2 pmol bacteriorhodopsin (60 ng purple membrane) sample was prepared by drying a 1-μL droplet of a suspension of purple membrane fragments (50 μg/mL) onto the thinnest portion of the waveguide. As shown in 4B, the three (3)

strongest bands near 1650, 1550, and 1200 cm^{-1} are due to amide I, amide II, and amide III vibrations, respectively. and are characteristic of the peptide backbone.

In comparison to prior art spectra of similar samples obtained using an IR microscope with planar waveguides 30-50 μm in thickness, the spectra of Figure 4 have substantially improved signal-noise ratios for 10-20× shorter measurement times. For example, the noise level in both of the spectra of Figure 4 (obtained with 500 scans each) is 0.001 absorbance units, whereas in spectra obtained with the microscope-coupled planar waveguides, the noise level was typically 0.01 absorbance units for 10,000 or 20,000 scans.

At the same time, the absorbance signals are somewhat reduced (between 3- and 5-fold) for similar sized samples on the tapered 20-μm waveguide, as opposed to the untapered 30-μm waveguides with 45° bevels used previously in the prior art. The reduction in attenuation signals is due to the predominance in the tapered waveguide of light propagating at relatively low off-axis angles, i.e. angles that lie less than 45° away from the waveguide surface plane. Light in such modes is absorbed relatively inefficiently by molecules at the surface, giving rise to smaller attenuation signals per molecule.

The principal advantage of tapering thin Ge planar waveguides is to permit a substantial increase in throughput for a given sensor thickness, making it possible to detect the IR signal level more precisely in a shorter length of time. The increase in throughput results from filling the large numerical aperture of a high-index waveguide medium (Ge, n=4). With an untapered planar waveguide, the largest numerical aperture that can be attained inside the waveguide is equal to the numerical aperture of the element that focuses light through air onto the end of the waveguide.

On the other hand, the largest numerical aperture that can be propagated through a tapered waveguide is determined by the refractive index of the waveguide material and it's

cladding, and is equal to $(n_1^2-n_2^2)^{½}$. Here n_1 is the refractive index of the waveguide medium (n_1=4 for Ge), while n_2 is the highest refractive index of the cladding materials in contact with the waveguide (n_2 = 2.26 for ZnS). For our ZnS-clad Ge waveguide, this maximum numerical aperture is 3.3. Thus, ~4-fold more light energy can be propagated through the sensing region of a planar Ge waveguide than can be obtained by focusing light through air into the (untapered) waveguide edge.

Gradually tapering a waveguide enables an increase in the numerical aperture. In such a taper, the product of the numerical aperture and waveguide thickness remains constant, as long as the maximum numerical aperture of the waveguide is not exceeded. A cone of light with numerical aperture of 0.3 that is transmitted into a 1-mm thick Ge waveguide maintains that numerical aperture across the air/Ge interface. Inside the Ge, it has a half- angular spread of only arcsine (0.3/4)=4°. It is possible to achieve a numerical aperture of 3.3 by gradually tapering the waveguide by a factor of about10. That is, once a waveguide thickness of about100 μm is reached, the numerical aperture of the waveguide is filled. At this thickness, the cone of propagating light rays extends all the way to the critical angle between Ge and ZnS, that is, to a half-angular spread of arcos (2.26/4)=56°.

The taper factor used herein (1 mm/20 μm=50) is much larger than the ratio of the maximum numerical aperture of the waveguide (3.3) to the numerical aperture of the input focusing optic (~0.3). This excess taper factor is intended to guarantee that, to the greatest extent possible, the numerical aperture of the sensing region of the waveguide is filled. With the particular light source present in the Midac spectrometer used herein, it is not difficult to fill the 1×1 mm input aperture of the tapered waveguide. Thus, a significant fraction of the input light is expected to be coupled out of the waveguide, i.e. to exceed the critical angle, as the waveguide is tapered down to its minimum thickness. It should be noted that the optimum apex to nadir ratio is dependent upon the detector size and shape

and, when taken in conjunction with the teachings herein, will be apparent to those skilled in the art.

Much of the light that goes into one end of the waveguide is lost as it travels into the middle (thinnest) portion of the waveguide, but then as the light travels into the region where the waveguide tapers outward again, there is no further loss of light energy (or flux). The loss of light is therefore not due simply to the presence of non-parallel surfaces; but more specifically to the presence of surfaces that converge to a thickness less than 1/4 of the input thickness. That is, nearly all the light present in the tapered region reaches the output face of the waveguide.

From here, the light is efficiently focused onto the 100-μm×100 μm area of the HgCdTe element in the Remspec detector. The use of an immersion lens in this detector provides an efficient coupling method that is extremely insensitive to the position of the fiber (or waveguide) output end. This greatly simplifies waveguide alignment, relative to the procedures that were required previously with a microscope. When incorporating a microscope, the output end of the waveguide had to be positioned at the very small focal area of the microscope's objective since the IR signal could be lost entirely with a mispositioning of as little as 50 μm.

The 1-mm width of the waveguide used in the example herein was chosen as the minimum width that could be easily manipulated without breaking. The thickness at the ends in these examples is the same as the width to match the square shape of the IR detector element used in the testing. The prism was then tapered as stated heretofore. Various taper ratios were tested with the result that the greater the thickness, the lower the sensitivity. A minimum 0.1-mm thickness, which corresponds to a taper ratio of 10, gave a high light throughput, but a lower (at least 5-fold) sensitivity to analyte at the surface

than the 20μm thickness. Test data (not shown) showed a continuous increase in sensitivity as the thickness of the waveguide decreased.

The wide range of propagation angles present at the sensing area of the tapered quasi-planar waveguide eliminates the distracting oscillatory transmission pattern that is observed for thin planar Ge waveguides. This is advantageous for a sensor, because it means that there are no sharp features in the spectrum that could be mistaken for absorption bands of a material present at the waveguide surface. Furthermore, the transmitted intensity at any frequency is not nearly as sensitive to waveguide alignment as with true planar waveguides.

The wide range of propagation angles present can lead to some degree of non-linearity of the absorbance signal, presenting small deviations from logarithmic response (i.e. the absorbance nonlinearities). In particular, the nonlinear response is not important for measurement of different spectra of samples that are subjected to an in situ perturbation while they are adsorbed or adhered to the surface of the waveguide. Additionally, the nonlinear response can be unimportant if there is a single known analyte, and a calibration curve can be established.

With the tapered waveguide, most of the internal reflections occur within a fairly small region near the point of minimum thickness. Thus, molecules located at the surface of this region predominate in the attenuation spectrum. This is a particular advantage for obtaining ATR spectra of small samples that must be kept submerged under water, e.g. biological samples. A relatively large pool of aqueous buffer can cover the surface of the entire waveguide and its supporting quartz substrate. Even when the entire waveguide is covered, this produces only about as much background attenuation as is shown in Figure 4A, i.e. maximally 0.2-0.3 absorbance units. Meanwhile, a biological sample that covers

only the ~1 mm^2 area above the thinnest portion of the waveguide can be detected and analyzed with great sensitivity.

The disclosed coupling method enables measurement of ATR-IR spectra using <100-μm thick planar waveguides in a horizontal configuration. The 20 μm thick waveguide affords high attenuation values for a small number of IR- absorbing molecules at the waveguide surface. This, and the improvement in signal/noise ratio obtained as a result of the coupling efficiency, make tapered Ge waveguides particularly well suited for measuring spectra of small biological samples, such as the detection of different spectra from various components of the cell membranes of individual frog eggs, 1.5 mm in diameter, that must be submerged under a bulk aqueous buffer.

The quasi-tapered waveguide 200 illustrated in Figure 5 is tapered as set forth above. The arcuate surface of the Ge prism 202 is then coated with a ZnS coating 204 and embedded into an epoxide substrate 208.

In Figure 6 the graphed spectra illustrates the comparison between Scotch® Tape, rubber cement and acetone. The spectra were read using the waveguide 200 having a 12 μm waveguide nadir. As can be seen in the graph, the Scotch® Tape 300 and the rubber cement 302 have similar spectra, showing that the tape is invisible and that the only material readable is the adhesive. The acetone spectrum 304 , however, provides a completely different spectrum reading than the two adhesives.

In Figure 7 the absorbance spectrum of D_2O, using the waveguide arrangement of Figure 5, is compared at different waveguide thickness. As illustrated, the sensitivity of the waveguide increased dramatically when using a 12μm waveguide. The overall sensitivity increase is substantially greater than the increase between the 70μm and 30μm readings.

Figure 9 illustrates the spectra of halorhodopsin using the 12μm waveguide of Figure 5.

What is claimed is:

1. A quasi-planar waveguide, said waveguide having a first surface, a second surface and a perimeter, said first surface having an arcuate contour and said second surface being planar, at least one of said first surface and said second surface being coated with a cladding, wherein said first surface is concave relative to said second surface.
2. The waveguide of claim 1 wherein said first surface and said second surface are substantially parallel.
3. The waveguide of claim 1 wherein said perimeter is comprised of multiple opposing planar surfaces, said perimeter surfaces being at right angles to said second surface.
4. The waveguide of claim 1 wherein said clad surface is adhered to a substrate, said substrate having a perimeter at least equal to said waveguide perimeter and having a thickness sufficient to support said waveguide.
5. The waveguide of claim 1 wherein said waveguide is made from single-crystal germanium.
6. The waveguide of claim 1 wherein said arcuate surface has an apex at least about four times greater than said surface nadir.
7. The waveguide of claim 1 wherein said waveguide is coupled directly to an IR detector.
8. The waveguide of claim 7 wherein said waveguide is mounted horizontally.
9. The waveguide of claim 1 wherein said waveguide has a nadir of less than 100μm.
10. The waveguide of claim 9 wherein said waveguide has a nadir of less than 20μm.
11. The waveguide of claim 10 wherein said waveguide has a nadir of about 1μm.
12. The waveguide of claim 1 wherein said cladding is ZnS.
13. The waveguide of claim 1 wherein said arcuate surface is polished to about a 0.1 μm finish.

14. The waveguide of claim 1 wherein said arcuate surface has a ratio of nadir to apex taper of at least about10.

15. The waveguide of claim 14 wherein said arcuate surface has a ratio of nadir to apex taper of up to about 50.

16. A quasi-planar waveguide, said waveguide being a single-crystal germanium, said waveguide being coupled directly to an IR detector and having:

   a. a first surface, said first surface having an arcuate surface with an apex about four times thicker than said surface's nadir, said arcuate surface having a taper of about10

   b. a second surface, said second surface being coated with a cladding and adhered to a substrate, said substrate having a perimeter at least equal to said waveguide perimeter and having a thickness sufficient to support said waveguide

   c. a perimeter, said perimeter being comprised of multiple opposing planar surfaces, said perimeter surfaces being at right angles to said second surface

wherein said waveguide increases IR signal throughput by filling the large numerical aperture thereby increasing the aperture to at least 1.

17. The method of producing a quasi-planar waveguide having a first surface, a second surface and a perimeter form of multiple opposing planar surfaces at right angles to said second surface, comprising the steps of:

   a. coating said second surface with a cladding;

   b. adhering said second surface to a substrate having a perimeter at least equal to said waveguide perimeter and a thickness sufficient to support said waveguide;

   c. grinding said first surface to a width proximate said nadir;

   d. minimizing light scattering by polishing said first surface to about a 0.1 μm

e. coupling directly to an IR detector

f. passing light from a light source, through said waveguide, to said IR detector;

wherein said waveguide increases IR signal throughput by about 4 fold by filling the large numerical aperture thereby increasing the aperture to at least 1.

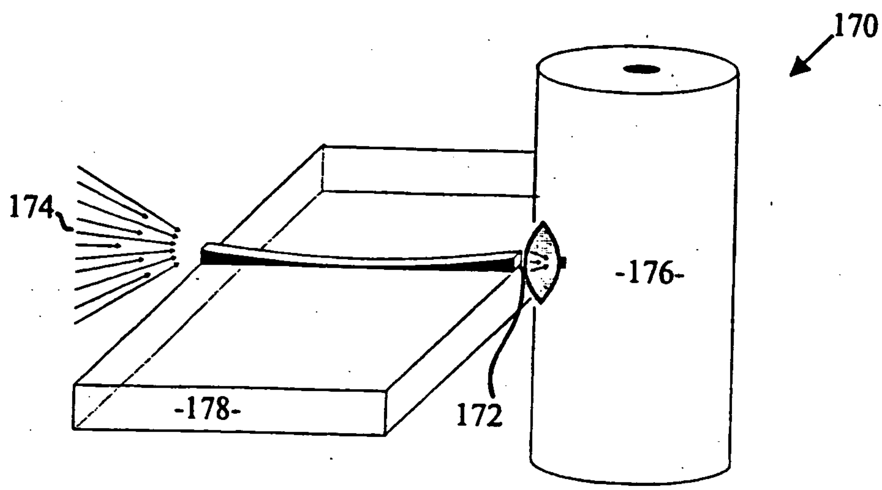


Figure 1

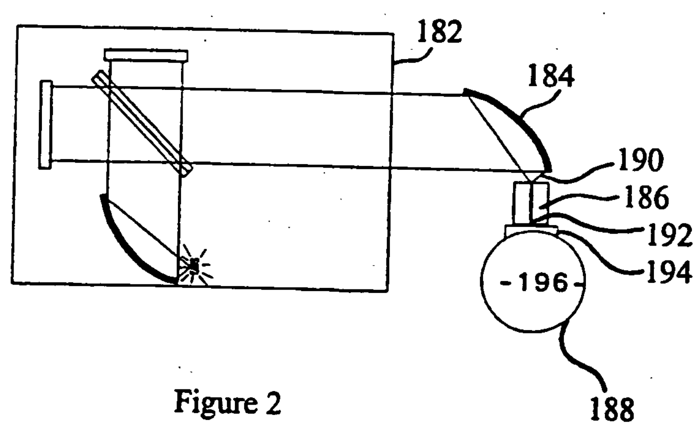


Figure 2

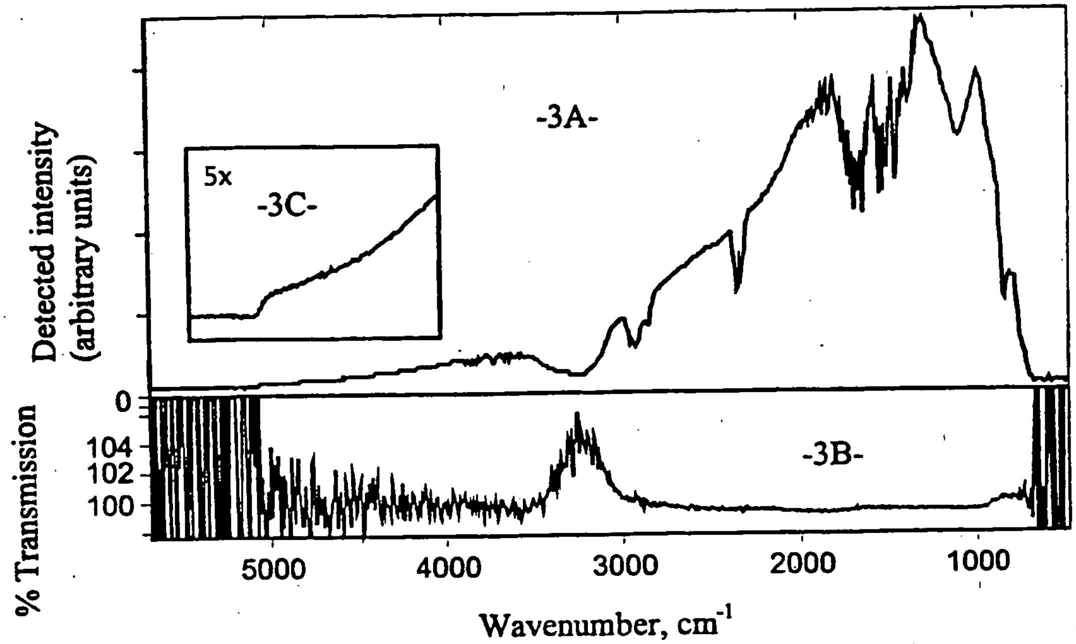


Figure 3

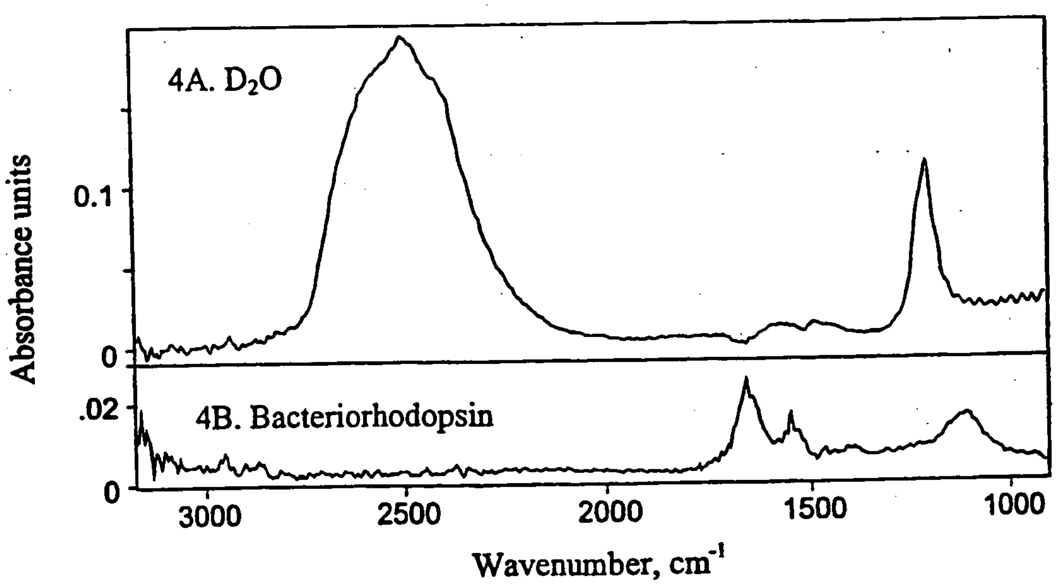


Figure 4

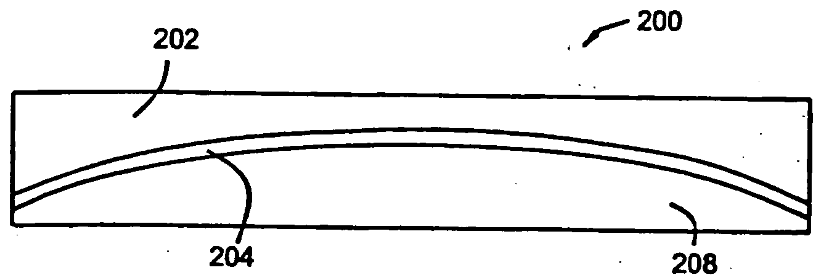


Figure 5

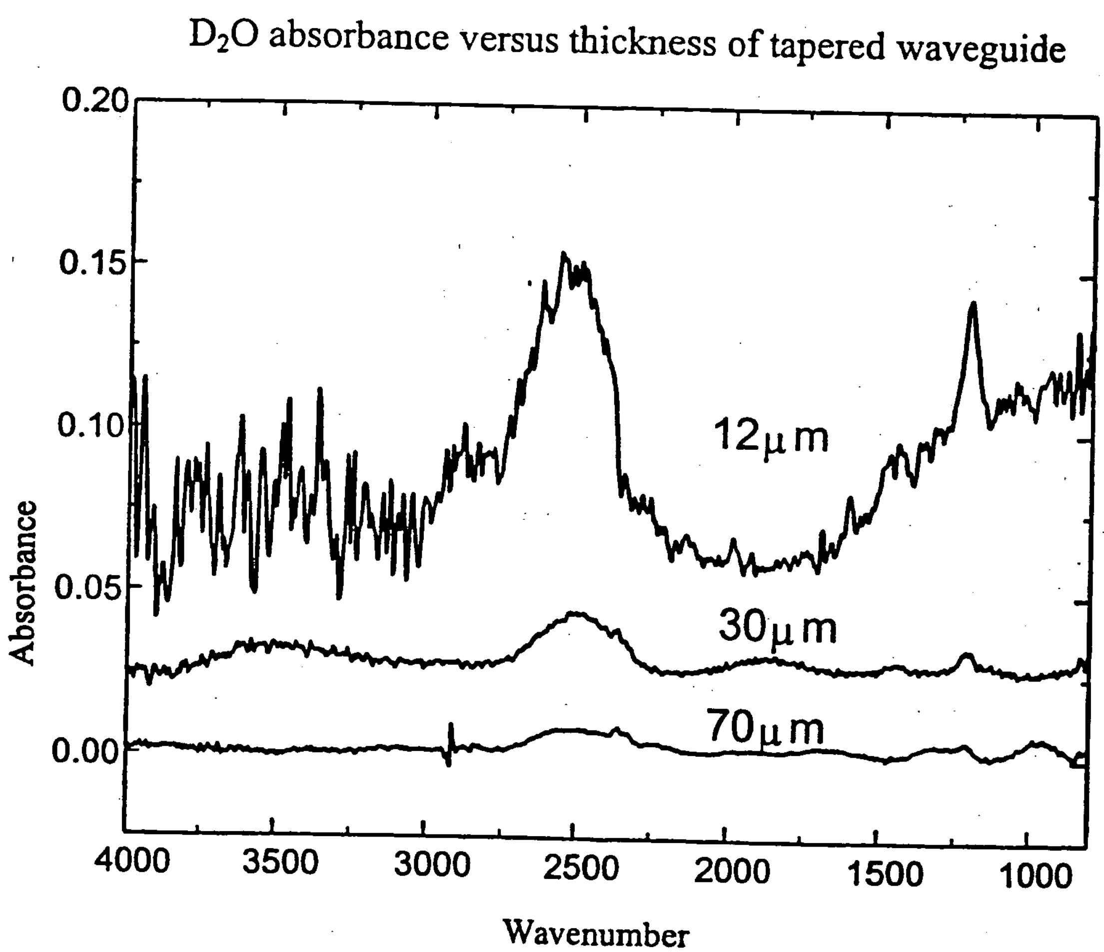
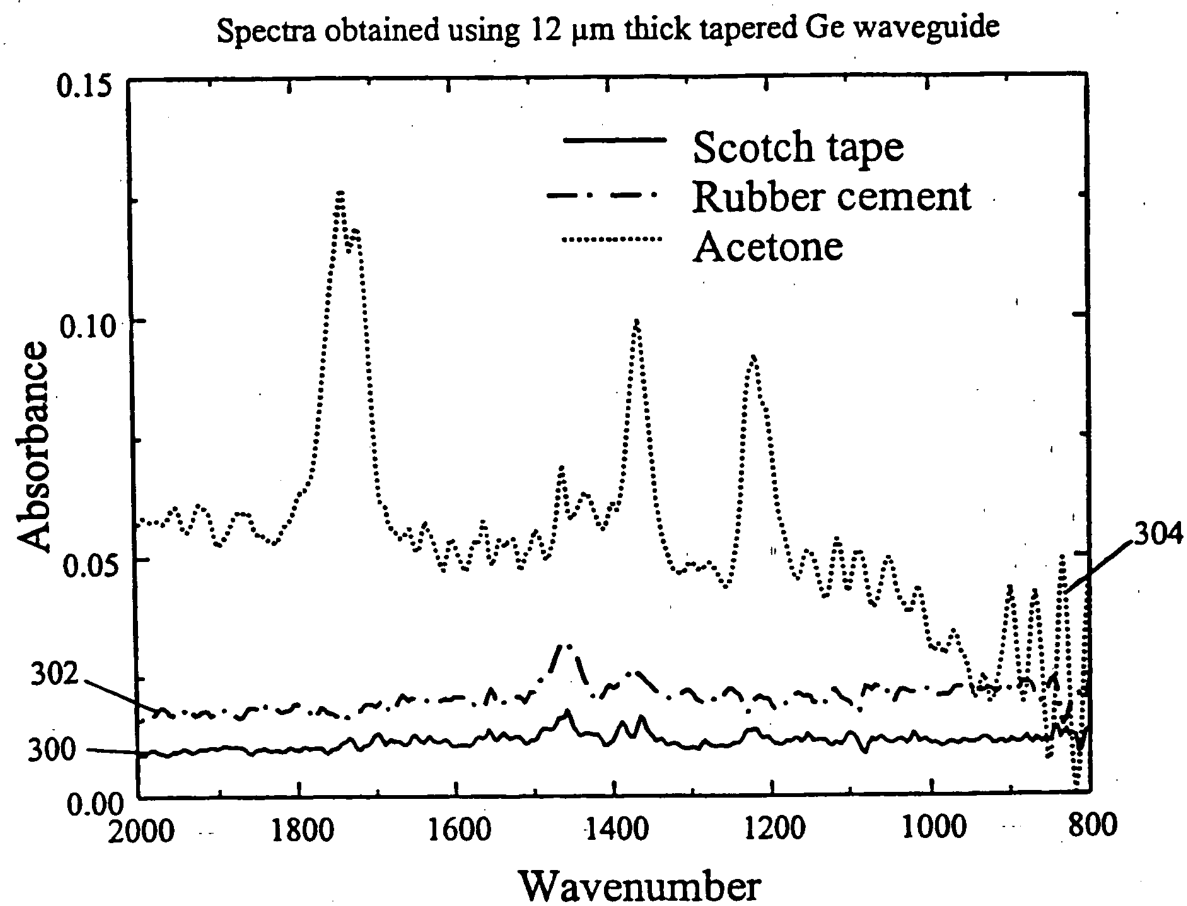


Figure 7



Spectra obtained using 12 μm thick tapered Ge waveguide
Scotch tape
Rubber cement
Acetone
Absorbance
0.15
0.10
0.05
0.00
302
300
304
2000
1800
1600
1400
1200
1000
800
Wavenumber

Figure 6

Spectra of halorhodopsin obtained using 12 μm thick tapered Ge waveguide

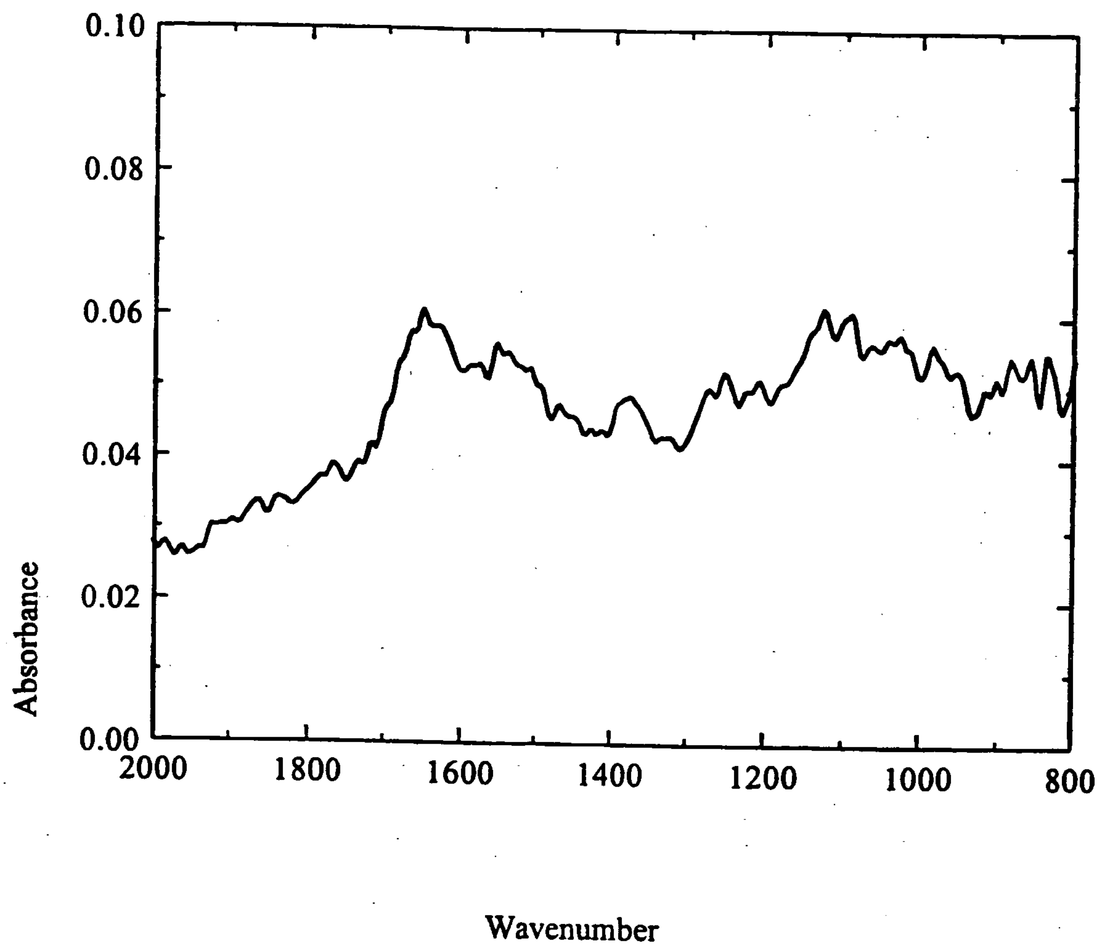


Figure 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/24974

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :GO2B 6/10; GOIN 21/00
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,980,831A (BRAIMAN ET AL.) 09 NOVEMBER. 1999 (09.11.99), SEE FIGURE 1 AND ENTIRE DOCUMENT	1-17
A	US 5,949,942 A (O'Connor) 07 SEPTEMBER 1999 (07.09.99) SEE FIG. 1, AND ENTIRE DOCUMENT	1-17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 31 JANUARY 2000	Date of mailing of the international search report 16 FEB 2000
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 308-7724	Authorized officer PHAN T. H. PALMER Telephone No. (703) 308-4848

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/24974

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

385/129, 12, 23
422/82.11

B. FIELDS SEARCHED
Minimum documentation searched
Classification System: U.S.

385/129, 12, 123, 130-132, 147
422/82.11
250/339.12

Form PCT/ISA/210 (extra sheet)(July 1992)*